



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED  
LAWRENCE  
BERKELEY LABORATORY

JUN 5 1981

LIBRARY AND  
DOCUMENTS SECTION

## Materials & Molecular Research Division

Submitted to the Journal of Molecular Structure

APPROACHING THE HARTREE-FOCK LIMIT FOR  
ORGANOTRANSITION METAL COMPLEXES

Henry F. Schaefer III

September 1980

### TWO-WEEK LOAN COPY

This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 6782



LBL-11973  
c.2

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

APPROACHING THE HARTREE-FOCK LIMIT  
FOR ORGANOTRANSITION METAL COMPLEXES

Henry F. Schaefer III

Department of Chemistry and Institute for Theoretical Chemistry

University of Texas

Austin, Texas 78712

and

Department of Chemistry and Lawrence Berkeley Laboratory

University of California

Berkeley, California 94720



### Abstract

In theoretical studies of the electronic structure of organometallic complexes, the choice of basis set is critical, much more so than for analogous studies of molecules containing only H, C, N, and O. This problem is discussed in light of structural predictions for the transition metal hydrides  $MH$ ,  $MH_2$ , and  $MH_4$ , for the fluorides  $MF_2$  and  $MF_3$ , for  $Ni(CO)_4$ ,  $Ni(C_2H_4)_3$ ,  $(CO)_3NiCH_2$ , and  $Ni(C_5H_5)_2$ .

## Introduction

Over the past three decades the study of organometallic molecules has moved from the periphery to the very heart of contemporary chemistry (1). Moreover, there is a growing awareness that the organometallic area is related to fields of research in the past considered rather applied, but now recognized as pertinent to society's energy needs. For example, we presented a thesis (2) four years ago that the transition metal-organic fragment chemical bond is the key to understanding the "fuzzy interface between surface chemistry, heterogenous catalysis, and organometallic chemistry." And in fact recent experiments (3,4,5,6) are beginning to confirm the notion that species such as  $\text{CH}$ ,  $\text{CH}_2$ ,  $\text{CH}_3\dot{\text{C}}\text{H}$ , and  $\text{CH}_2=\text{C}:$  play important roles on metal surfaces and in clusters. Since these sorts of model organometallic species (e.g.  $\text{Fe}_3\text{CH}_2$ ) are often unstable and very difficult to prepare in the laboratory, the need for theoretical studies is apparent.

In the course of our efforts (and those of others) to examine theoretically the sort of organometallic species described above, it became apparent that certain technical problems occur for transition metals which are not present for molecules composed exclusively of H, C, N, and O atoms. The present review is primarily concerned with the problem of basis set incompleteness at the single configuration Hartree-Fock level of theory. Since the ultimate reliability of electronic structure predictions depends on the choice of basis set (7), such a topic is quite appropriate to the present volume.

Two decades ago, in the early days of ab initio molecular electronic structure theory, the Laboratory for Molecular Structure

and Spectra (LMSS) at the University of Chicago was perhaps the most important center of this new area of research (8). The ab initio studies at LMSS were primarily directed by C. C. J. Roothaan, and in this author's opinion, Roothaan's strong leadership provided an orderly structure which has been of immense and continuing benefit. Specifically, Roothaan and his colleagues (especially Cade) insisted that the Hartree-Fock limit be approached as closely as possible for the diatomic molecules under discussion (9). Many questioned the judgment of this philosophy, since lower total energies (and hence "better" wavefunctions in the variational sense) are obtained by appending configuration interaction (CI) to considerably more modest basis sets than those used by Roothaan and co workers. What became crystal clear from the early research at LMSS was exactly how good the Hartree-Fock method was in predicting many of the properties of diatomic molecules containing atoms lighter than argon (10). Bond distances were found to be quite satisfactorily reproduced by these near Hartree-Fock studies, being typically a few hundredths of an angstrom shorter than experiment. However, it was also discovered that diatomic dissociation energies are almost inevitably severely underestimated by extended basis set self-consistent-field (SCF) studies. The great virtue of these LMSS studies was that comparison with experiment provided an immediate gauge of the importance of electron correlation. Once the quantitative role of correlation effects on molecular predictions had been established, subsequent researchers were able to go about the critical task of developing methods (11) for the description of electron correlation. In addition the stage was set for analogous systematic studies of polyatomic molecules, as exemplified by the Carnegie-Mellon research group of J. A. Pople in the early 1970's (12).

For a variety of reasons, systematic studies (in the Roothaan-Pople sense) of transition metal species have never been carried out. Perhaps quite obviously, the most interesting classes of molecules, e.g.  $\text{Fe}(\text{C}_5\text{H}_5)_2$  and  $\text{Ni}(\text{CO})_4$ , are even

today too large to allow the very close approach to the Hartree-Fock limit that was possible (9) for  $N_2$  and  $N_2^+$  in 1966. However systematic studies with smaller basis sets would have been feasible. Secondly, the research groups at the forefront of the theoretical study of transition metal species have been much more interested in chemistry than in ab initio methodology. Nevertheless, as computational technology makes theoretical studies of organometallic species more routine, it is expected that such systematic studies will begin to appear. At the present time, for example, W.J. Hehre ( University of California, Irvine) is engaged in such an investigation.

Over the past eight years, we have maintained a modest but continuing interest in transition metal species. In light of the above introductory remarks, it will not surprise the reader that our research has emphasized the use of relatively large basis sets and typically not attempted to go beyond the Hartree-Fock limit. Our philosophical bent with respect to transition metal systems becomes all the more apparent when it is noted that much of our research on molecules composed exclusively of H, C, N, and O atoms has involved state-of-the methods for obtaining highly correlated wave functions (13). Here, then, we review briefly what might be described as near-Hartree-Fock studies of molecules containing transition metal atoms.

#### Choice of Basis Sets

For a primitive gaussian basis set of a given size to be most effective with respect to the total energy, the orbital exponents  $\alpha$  must be variationally optimum. Although this optimization could take place at the molecular level, the expense is typically prohibitive and atomic optimizations are carried out. For transition metal atoms, fairly widely used gaussian basis sets of this type have been reported by Wachters (14), and by Roos, Veillard, and Vinot (15). Although



we have occasionally used the smaller Roos basis sets in the study of systems such as  $Mn-CH_2$  (16), all the research discussed herein employed the larger Wachters basis sets.

The original Wachters basis sets for the first row transition metal atoms may be labeled M (14s 9p 5d) and yield atomic SCF energies within 0.1 hartree of the appropriate Hartree-Fock limits. However, being optimized for the  $4s^2 3d^n$  electron configurations, these basis sets do not describe the 4p orbital (unoccupied in the atom). Therefore it is appropriate to append one or more p basis functions with smaller orbital exponents (i.e. greater spatial extent) for molecular studies. In the studies reviewed here, one (17,18), two (19,21,22), or even three (20) sets ( $p_x, p_y, p_z$ ) of p functions have been added to the Wachters basis to describe the 4p metal orbital.

As early as 1971 Roos, Veillard, and Vinot (15) noted that atom-optimized transition metal 3d orbitals are quite contracted and recommended that an additional' more diffuse gaussian 3d function be appended to their (4d) sets. Several years later Swope (24) and Hay (25) independently recognized that the  $s^2 d^n$  configuration is artificially favored over the  $sd^{n+1}$  configuration with the Roos (15) and Wachters (14) basis sets. However, adding a single more diffuse primitive gaussian d function brings the predicted  $s^2 d^n - sd^{n+1}$  separations into satisfactory agreement with the numerical Hartree-Fock atomic results. Therefore, in our recent research, the Wachters (5d) sets have been extended to (6d) using the basis functions recommended by Hay (25). In hindsight it now seems apparent that while the 3d orbital of a transition metal atom is rather contracted, this 3d orbital takes on a much greater spatial extent when several carbonyl groups approach to form a typical organometallic molecule such as  $Ni(CO)_4$ .

To be effective in molecular studies a basis set such as that described above must be flexibly contracted (26). Adopting the standard segmented procedure, Wachters (14s 9p 5d) set may be contracted to (10s 6p 2d) with very little loss in energy relative to the completely uncontracted set. We recommend that this basis be augmented with one additional p function (essentially to describe the metal 4p orbital)

and one additional d function to describe the expansion of the 3d shell associated with molecule formation. Such a basis set is roughly of "triple zeta" quality and may be designated M(14s 10p 6d/10s 7p 3d).

Before leaving this section, a final problem concerning the  $s^2d^n - sd^{n+1}$  energy separation in transition metal atoms should be mentioned. That is, even after reaching the Hartree-Fock limit, this energy difference is predicted quite incorrectly. For example, in nickel the Hartree-Fock separation between the  $s^2d^8\ ^3F$  and  $sd^9\ ^3D$  states is 1.28 eV, while the experimental value is -0.03 eV (25). Inasmuch as gas-phase experimental studies of species such as  $MCH_2^+$  are now beginning to appear (27), it can be quite important to predict the correct electronic ground state for the transition metal atom (16,24). Perhaps the simplest satisfactory solution to this problem has recently been given by Dunning, Botch, and Harrison (28). They noted that for the  $sd^{n+1}$  configuration, the constraint that all (n+1) d electrons occupy the same spatial orbital is a serious one. A more realistic description, obtained via a two-configuration (at least for the case of titanium) SCF procedure, allows a substantial measure of  $sd^n d^1$  character to be introduced into the wavefunction. The same sort of correction is much less important for  $s^2d^n$  states and its use appears to provide a still relatively simple but realistic approach to the theoretical prediction of the  $s^2d^n - sd^{n+1}$  energy difference.

An equivalent description of the  $d^{n+2}$  electron configuration logically requires even more incorporation of diffuse 3d character (28). These atomic observations are helpful in the sense that the  $d^{n+2}$  electron configuration is conventionally thought to characterize most organometallic species (1). The spatially extended nature of the  $d^{n+2}$  atomic state thus serves to re-emphasize (15,16,24,25) the necessity for diffuse (relative to those required in atomic  $s^2d^n$  basis sets) d functions in organotransition metal basis sets.

### Transition Metal Halides

The first transition metal system studied (17) in our laboratory was  $\text{ZnF}_2$ , for the purpose of obtaining a Walsh diagram for bending. The hope was that this single diagram might serve as a guide to understanding the bond angles of the other transition metal difluorides, several of which have been observed experimentally.  $\text{ZnF}_2$  is known from electric deflection studies (29) to be linear and the theoretical predictions confirmed this result.

The valence molecular orbitals of  $\text{ZnF}_2$  fall in two distinct groups. The orbitals of atomic d parentage lie in a narrow range of orbital energies, namely -0.872 to -0.858 hartrees. These d-like orbital energies all increase as the molecule is bent from the linear conformation ( $\theta = 180^\circ$ ) to  $\theta \sim 100^\circ$ , indicating that as far as these five MO's are concerned, linear equilibrium geometries are favored. The six highest occupied MO's of  $\text{ZnF}_2$  are presented in a Walsh diagram in Figure 1. These are the remaining occupied valence orbitals, constructed from Zn 4s, 4p and F 2s, 2p AO's.

Figure 1 suggests that the only hope for bent electronic states of the transition metal difluorides lies with the  $10a_1$  orbital, which prefers (in the Walsh sense) a bond angle of  $\sim 140^\circ$ . It is also clear that the best hope for a bent equilibrium geometry will occur for the early transition metals, for which d-like MO energies will lie much higher relative to the six orbitals in Figure 1. Since occupation of the d orbitals is a contributor to linearity, a molecule such as  $\text{TiF}_2$  will have a much better chance of being bent than  $\text{ZnF}_2$ . And, in fact, recent spectroscopic studies by Devore and Weltner (30) suggest that  $\text{TiF}_2$  does have a bent structure.

The trifluorides  $\text{ScF}_3$ ,  $\text{TiF}_3$ ,  $\text{CrF}_3$ , and  $\text{FeF}_3$  have all been observed spectroscopically and this combined with our prior interest in the difluorides led to an examination of the  $\text{FeF}_3$  molecule (18). Again, the motivation was to construct a single Walsh diagram from which to survey the entire series of first-row transition

metal fluorides. The high-spin  ${}^6A_1'$  state was predicted to be the ground state and has a planar equilibrium geometry.

At the time the  $\text{FeF}_3$  research was carried out (1972) it was quite a surprise to find that the half-occupied  $1e''$ ,  $6a'$ , and  $5e'$  orbitals had orbital energies well below the fully occupied  $7a_1'$ ,  $6e'$ ,  $7e'$ ,  $2e''$ ,  $3a_2''$  and  $1a_2'$  orbitals. That is, the simple notion that partially occupied orbitals lie closer to the Fermi surface than fully occupied orbitals was completely reversed among the valence orbitals of  $\text{FeF}_3$ . Eight years later we have seen many more examples (16,19,21,24,31) this behavior and recognize it as a consequence of the shell structure of the transition metal atom. For molecules such as  $\text{MX}_2$  and  $\text{MX}_3$  the d-like molecular orbitals are split relatively little by the ligand field, and accordingly their orbital energies lie in a very narrow band. Thus the fact that the d-like half-occupied MO's lie below the fully occupied valence orbitals is no more surprising than the observation that in the manganese atom it requires 14.2 eV to remove an electron from the half-occupied 3d orbital, while removal of an electron from the fully occupied 4s orbital requires only 7.4 eV.

A Walsh-like sketch of the 3d-like orbital energies of  $\text{FeF}_3$  is given in Figure 2. There it is seen that pyramidalization increases the one-electron energies, although the changes are very small between the planar ( $120^\circ$ ) and tetrahedral ( $109.47^\circ$ ) geometries. Since the other valence orbital energies also increase with pyramidalization, it is not unreasonable to suggest that the entire series of  $\text{MF}_3$  molecules may be planar or nearly planar. This suggestion has been pursued in the very fine research of Yates and Pitzer (32). Yates and Pitzer used the same large Wachters basis set as Hand (18) except that two (rather than one) sets of p functions were added to describe the metal 4p orbital.

The theoretical predictions of Yates and Pitzer for the series  $\text{ScF}_3$  to  $\text{NiF}_3$  are given in Table I. Consistent with the qualitative prediction of Hand, Hunt, and Schaefer (18), they found all the  $\text{MF}_3$  molecules except  $\text{CrF}_3$  to have

planar geometries. The sole exception was found to be nearly planar, exhibiting an F-Cr-F equilibrium angle of  $117^\circ$ . Perhaps the most impressive aspect of the Yates-Pitzer opus (32) was their ab initio prediction of the out-of-plane vibrational frequencies, also seen in Table I. The reliability of their near-Hartree-Fock predictions is confirmed by comparison between their theoretical frequency of  $129.6\text{cm}^{-1}$  for  $\text{ScF}_3$  and the experimental value  $119 \pm 10\text{cm}^{-1}$  of Hauge, Hastie, and Mrgrove (33).

### Transition Metal Hydrides

Our initial interest in this class of molecules was instigated by the fact that diatomic MH has the highest spin electronic ground state of any known molecule (34). The  $X^7\Sigma^+ - A^7\Pi$  transition of MH has been known for some time (35), and both electronic states were studied theoretically by Bagus and the present author (31). The SCF level of theory was used in conjunction with large Slater function basis sets, e.g.  $\text{Mn}(8s\ 7p\ 4d\ 2f)$ , essentially guaranteeing near-Hartree-Fock molecular results. Analogous to  $\text{FeF}_3$ , the  $3d$ -like molecular orbitals are half occupied and lie within a narrow energetic range below the doubly occupied  $6\sigma$  bonding orbital. In other words, the manganese atom  $3d^5$  configuration survives essentially unchanged in both electronic states of MH, and this is expected to be true of most of the other molecules from ScH to CuH. The predicted ground state spectroscopic constants are in encouraging agreement with experiment: for example  $r_e = 1.789\text{\AA}$  (expt.  $1.722\text{\AA}$ ),  $D_e = 1.57\text{ev}$  ( $2.4 \pm 0.3\text{ ev}$ ), and  $\omega_e = 1549\text{ cm}^{-1}$  (expt.  $1548\text{cm}^{-1}$ ). Thus it appears that the Hartree-Fock approximation is quite meaningful for this family of diatomic transition metal hydrides.

A more recent theoretical study (21) of the dihydrides  $\text{MH}_2$  was motivated by Weltner's spectroscopic determination that the  $^6A_1$  ground state of  $\text{MH}_2$  is bent, with a bond angle of  $\sim 120^\circ$  (36,37). this result did not appear consistent with our predictions for the difluorides  $\text{MX}_2$  (17), but then again it could be argued that

hydrogen and fluorine are so very different as ligands that any analogy between  $\text{MF}_2$  and  $\text{MH}_2$  is suspect. However, a more specific qualitative MO argument may be ventured for  $\text{MH}_2$ . If the  $3d_M - 1s_H$  interaction is weak for the elements of the series (Sc - Cu) then a linear geometry is expected for every  $\text{MH}_2$  molecule. This is based on a bonding scheme, in Figure 3, involving the interaction of the  $1s$  orbitals of the H atoms with the two  $4s-4p$  hybrid orbitals available from the transition metal.

Quantitative SCF studies using a large-basis set do in fact predict a linear geometry for  $\text{MnH}_2$  with  $r_e(\text{Mn-H}) = 1.754\text{\AA}$ . Configuration interaction (6089 configurations) confirms that correlation effects do not affect the prediction of linearity, with the linear geometry lying 3.0 kcal below the structure with  $\theta(\text{HMH}) = 150^\circ$ . As suspected, there is little interaction between the M  $3d$  and H  $1s$  orbitals, and as with  $\text{MF}_3$  (18) and  $\text{MH}$  (31) the half-occupied  $3d$ -like MO's lie energetically below the two doubly-occupied bonding orbitals  $6a_1$  and  $3b_2$ .

Our general prediction for  $\text{MX}_2$ ,  $\text{MX}_3$ ,  $\text{MH}_2$ , and  $\text{MH}_3$  is that these series of molecules are more likely to be bent ( $\text{MX}_2, \text{MH}_2$ ) or pyramidal ( $\text{MX}_3, \text{MH}_3$ ) as one traverses to the left of the periodic table amongst the first row transition metals. This was specifically tested by examining  $\text{TiH}_2$  at the same levels of theory applied to  $\text{MnH}_2$  (21). Due to the manifold of unoccupied  $3d$  orbitals for Ti, there are no fewer than ten plausible low-lying triplet electronic states. Among these the  $\dots 7a_1 8a_1 {}^3A_1$  state was well-described by a single configuration and in addition one of the best candidates (from an analysis of the  $\text{MnH}_2$  Walsh diagram) for a nonlinear equilibrium geometry.

The  ${}^3A_1$  state of  $\text{TiH}_2$  was found to be linear from both SCF and CI studies. However the energy difference between linear and bent structures is now so small that the notion of a well-defined equilibrium geometry becomes questionable. Specifically the energy difference between  $\theta(\text{HTiH}) = 140^\circ$  and  $\theta = 180^\circ$  is only

0.8 kcal. This result and those for  $\text{MnH}_2$  and  $\text{NiH}_2$  (38) are seen in Figure 4, which nicely illustrates the general trend discussed in the previous paragraph. The analogous trend toward increased "floppiness" in going from  $\text{NiF}_3$  to  $\text{ScF}_3$  is seen in the out-of-plane vibrational frequencies given in Table I.

There are only three series of transition metal molecules for which near-Hartree-Fock studies have been systematically reported. The first is the diatomic hydrides, for which we have the Oxford studies of Richards and his co-workers (39). Second is the  $\text{MF}_3$  series, for which the work of Yates and Pitzer (32) has been discussed here. Thirdly is the research of Hood, Pitzer, and the author (19) on the tetrahedral  $\text{MH}_4$  series. Their study of  $\text{TiH}_4$ ,  $\text{VH}_4$ ,  $\text{CrH}_4$ ,  $\text{MnH}_4$ ,  $\text{FeH}_4$ ,  $\text{CoH}_4$ , and  $\text{NiH}_4$  used very large basis sets, designated  $\text{M}(14s\ 11p\ 6d/10s\ 8p\ 3d)$ ,  $\text{H}(5s\ 1p/3s\ 1p)$ . In the course of deciding upon this basis, a considerable amount of experimentation was conducted on the known molecule  $\text{TiH}_4$  and some of this is summarized in Table II.

The near Hartree-Fock predictions for  $\text{MH}_4$  molecules are collected in Table III, in particular M-H bond distances, dissociation energies and electronic excitation energies  $T_e$ . It is interesting that the conventional correlation short bond  $\rightarrow$  strong bond is consistently contradicted in Table III. In fact the shortest  $\text{MH}_4$  bond for a ground electronic state occurs for  $\text{MnH}_4$  (1.577Å) which has the smallest predicted dissociation energy, -36 kcal for  $\text{MnH}_4 \rightarrow \text{Mn} + 4\text{H}$ . Experience tells us (7), of course, that the effects of electron correlation will increase these Hartree-Fock dissociation energies by perhaps as much as 1-ev (23 kcal) per electron pair bond. But the ordering of dissociation energies provided by the Hartree-Fock method should be meaningful.

A dissociation energy of -218 kcal is required for the absolute thermodynamic stability of  $\text{MH}_4$  relative to  $\text{M} + 2\text{H}_2$ . Of the seven  $\text{MH}_4$  molecules studied here, only  $\text{TiH}_4$  comes close to having a predicted dissociation energy this large. It should be emphasized, of course, that absolute thermodynamic

stability is by no means a prerequisite for the preparation and characterization of a molecular species.

In this light, we suspect that  $\text{VH}_4$  and  $\text{CrH}_4$  could be prepared in the laboratory, in the near future, under appropriate conditions. The remaining four molecules  $\text{MnH}_4$ ,  $\text{FeH}_4$ ,  $\text{CoH}_4$ , and  $\text{NiH}_4$  will probably remain hypothetical for the indefinite future, unless some alternate geometry (e.g., square planar) should prove energetically more favorable. Their hypothetical nature notwithstanding, molecules such as  $\text{CoH}_4$  should still be considered as reasonable zeroth order molecules for the more complicated stable transition metal alkyls (40) such as  $\text{Co}(\text{l-norbornyl})_4$ .

One intuitively expects (41) the Hartree-Fock approximation to be a better one for high spin systems than for the comparable closed-shell molecular states. To explicitly test the magnitude of this differential correlation effect, it was decided to examine the vertical  $^5\text{T}_2 - ^1\text{A}_1$  energy separation for  $\text{FeH}_4$  in more detail. CI including all single and double excitations reduces the Hartree-Fock energy separation of 23 kcal by 18 kcal. Higher order correlation effects (42) will reduce this quintet-singlet separation by a few more kcal, so it is likely that the  $^5\text{T}_2$  and  $^1\text{A}_1$  states of  $\text{FeH}_4$  are nearly degenerate. Analogous arguments may be applied to correct the other Hartree-Fock excitation energies given in Table III.

### Genuine Organometallic Species

Having accumulated a fair amount of experience on the above-discussed transition metal halides and hydrides, it was deemed judicious to proceed to near Hartree-Fock studies of systems of more widespread interest, namely simple organometallic systems.

#### A. Nickel Tetracarbonyl

This and subsequent research (22) on  $(\text{CO})_3\text{NiCH}_2$  were carried out in collaboration with several staff members of the National Resource for Computation



in Chemistry (NRCC).  $\text{Ni}(\text{CO})_4$  is of course one of the classic organometallic molecules and unlike the vast majority, its gas-phase geometrical structure is known from experiment. The early (1935!) electron diffraction study of Brockway and Cross (43) determined a tetrahedral structure with  $r(\text{Ni}-\text{C}) = 1.820 \text{ \AA}$ ,  $r(\text{C}-\text{O}) = 1.150 \text{ \AA}$ . Last year Hedberg, Iijima, and Hedberg (44) reported a refined electron diffraction structure, with  $r(\text{Ni}-\text{C}) = 1.838 \text{ \AA}$ ,  $r(\text{C}-\text{O}) = 1.141 \text{ \AA}$ . Therefore  $\text{Ni}(\text{CO})_4$  provides a good opportunity to test the reliability of near-Hartree-Fock geometrical predictions for organotransition metal species.

In the work of Spangler, Wendoloski, Dupuis, and Chen (22) a large basis set, designated  $\text{Ni}(15s\ 11p\ 6d/11s\ 8p\ 3d)$ ,  $\text{C}, \text{O}(9s\ 5p/4s\ 2p)$ , was employed. SCF optimization of the geometry of  $\text{Ni}(\text{CO})_4$  yielded  $r_e(\text{Ni}-\text{C}) = 1.884 \text{ \AA}$ ,  $r_e(\text{C}-\text{O}) = 1.139 \text{ \AA}$ . The latter CO distance is in essentially perfect agreement with experiment (44),  $1.141 \text{ \AA}$ . However, the Ni-C distance is  $0.046 \text{ \AA}$  longer than experiment. This is perhaps surprising, since the typical effect of electron correlation (in molecules composed exclusively of H, C, N, and O atoms) is to further lengthen predicted Hartree-Fock bond distances. If the true Hartree-Fock Ni-C bond distance is  $\text{Ni}(\text{CO})_4$  is significantly less than the value  $1.884 \text{ \AA}$  seen here, it is probably due to the absence in our basis of d functions on the C and O atoms. A less likely contributor is the absence of polarization functions (in this case f functions) on the nickel atom. In any case, good qualitative agreement with experiment has been obtained from what is perhaps the first complete organometallic geometry optimization using a large basis set.

#### B. Tris ( $\eta^2$ -Ethylene) Nickel (0)

One of the most remarkable organometallic species synthesized in recent years is the tris ( $\eta^2$ -ethene)nickel(0) molecule (45). This was the first transition-metal complex prepared in solution with ethylenes alone as its ligands. In 1973 Fischer, Jonas, and Wilke prepared  $\text{Ni}(\text{C}_2\text{H}_4)_3$  in a diethyl ether solution, which was found to be pale yellow in color. Upon crystallization from solution at 195 K

they obtained colorless needle-shaped crystals. Fischer, Jonas, and Wilke assumed the molecule to have the "planar"  $D_{3h}$  structure seen in Figure 5 and reported nuclear magnetic resonance and infrared spectroscopic data consistent with this assumption.

Our attention was first drawn to tris(ethylene)nickel(0) by the excellent theoretical study of Rösch and Hoffmann (46). They elucidated the qualitative features of the electronic structures of  $Ni(C_2H_4)_n$  for  $n = 2, 3$ , and 4, and supported their findings with extended Hückel calculations. Rösch and Hoffman were able to predict the conformational preferences of both  $Ni(C_2H_4)_2$  and  $Ni(C_2H_4)_3$ . In the latter case, they found the planar structure to be favored by 17 kcal over the upright geometry of Figure 5.

As in the other studies reviewed here, our research (20) on  $Ni(C_2H_4)_2$  and  $Ni(C_2H_4)_3$  used an extended basis set derived from that of Wachters (14). In this way the SCF energy separation between the upright and planar conformations is 23.7 kcal, in qualitative agreement with the extended Hückel result (46). Equally encouraging is the fact that Rösch and Hoffmann predicted the twisted form of  $Ni(C_2H_4)_2$  to lie 1.5 kcal below the planar structure, while the large basis ab initio results place the two forms within 0.1 kcal. Thus there is reasonable evidence upon which to base a hope that extended Hückel will provide meaningful qualitative predictions for these sorts of conformational energy changes. The planar-upright energy separation in  $Ni(C_2H_4)_3$  was also determined using a smaller basis (15) of size  $Ni(10s\ 7p\ 5d/7s\ 6p\ 3d)$ . The predicted separation of 25.1 kcal is only 1.4 kcal greater than the more reliable theoretical result, suggesting that this barrier is not too sensitive to basis set size.

Perhaps the most intriguing prediction made for tris( $\eta^2$ -ethylene)nickel(0) is that its positive ion has the opposite equilibrium conformation from the neutral. That is, the upright conformer of  $Ni(C_2H_4)_3^+$  lies 2.4 kcal below the planar structure. Although initially a surprise, this energetic reversal upon ionization is readily explained using the Walsh diagram in Figure 6. The highest occupied molecular orbital

(HOMO) in Figure 6 strongly prefers the planar conformation, and this is indeed favored when the  $9e'$  orbital is fully occupied. However the two other orbitals seen in Figure 6 have a preference for the upright conformation, and the removal of one electron from the HOMO (i.e. ionization) is just enough to slightly favor the total energy of the upright conformation.

Before concluding it should be noted that the shape of the Walsh diagram in Figure 6 may be readily understood in terms of Ni 3d to olefin  $\pi^*$  donation (47). For the planar arrangement the three ethylene  $\pi^*$  orbitals transform as  $a_1' + e'$ , but for the upright conformation these  $\pi^*$  orbitals become  $e'' + a_1'$ . Thus the  $9e'$  orbital is the beneficiary of back bonding in the planar conformation. However, there are no  $C_2H_4$   $\pi^*$  orbitals of  $e'$  symmetry in the upright case, so the  $9e'$  orbital is pushed up energetically in going from the planar to the upright conformation. Conversely, the  $4e''$  orbital is favored energetically in the upright conformation, since only for the upright geometry do the  $\pi^*$  orbitals transform as  $e''$ . The same general line of reasoning suggests that the middle orbital in Figure 6 should have an essentially constant orbital energy. This is because the  $\pi^* C_2H_4$  orbitals may be used to construct a single  $a_1'$  symmetry orbital for either the planar or upright conformations.

### C. Methylene (Tricarbonyl) Nickel (0).

A critical ingredient in the flowering of organometallic chemistry over the past decade has been the synthesis and characterization of transition metal carbene complexes (48). This research began with the report in 1964 by Fischer and Maasböl (49) of methoxymethyl carbene (pentacarbonyl) tungsten. Although the notion of a double bond between transition metals and carbon was initially unorthodox, it is now very well entrenched and indeed an integral part of the thought patterns of organometallic researchers. In fact, metal carbene concepts borrowed from organometallic chemists are now being used in attempts to understand surface chemistry and heterogeneous catalysis (50,51).

From a theoretical perspective, the simplest realistic transition metal carbene might involve only CO ligands and the primitive  $\text{CH}_2$  or methylene itself. Furthermore, such prototype carbene complexes should fulfill the 18-electron rule (52). In this light, it becomes apparent that the simplest model transition metal carbenes of this type are

methylene(pentacarbonyl)chromium(0)



methylene(tetracarbonyl)iron(0)



and methylene(tricarbonyl)nickel(0)



None of these three molecules has been prepared to date in the laboratory, primarily because of the problems involved in incorporating the unsubstituted methylene as a ligand. In fact, the only organometallic complexes thus far reported with a mononuclear  $\text{M}=\text{CH}_2$  bond are Schrock's  $\text{Cp}_2\text{TaCH}_3\text{CH}_2$  molecule (53) and Schartz's  $\text{Cp}_2\text{Zr}(\text{PPh}_2\text{Me})\text{CH}_2$  (54). However, we would not be surprised to see successful syntheses of  $(\text{CO})_5\text{CrCH}_2$ ,  $(\text{CO})_4\text{FeCH}_2$ , and  $(\text{CO})_3\text{NiCH}_2$  during the next decade.

The same large basis set used above for  $\text{Ni}(\text{CO})_4$  was used in SCF studies (22) of the prototype nickel carbene. Our only reservation concerning this basis was the absence of a set of d functions on the carbene carbon atom. For the isolated  $\text{CH}_2$  biradical, d functions are very important in obtaining a reliable value of the singlet-triplet energy gap. However, preliminary work (22) on the naked  $\text{NiCH}_2$  molecule (55) showed that d functions together with the use of a larger carbon sp basis (10s 6p/5s 3p) increase the Ni-C bond distance by only 0.004 Å and the HCH angle by only 0.4°. A complete SCF geometrical optimization of  $(\text{CO})_3\text{NiCH}_2$  was not practical, so several reasonable assumptions (illustrated in Figure 7) were made.

The methylene angle in  $(\text{CO})_3\text{NiCH}_2$  was predicted to be  $108.2^\circ$  and the Ni-C bond distance  $1.831 \text{ \AA}$ . This small bond angle is certainly more reminiscent of singlet methylene ( $\theta \approx 102.5^\circ$ ) than the triplet state [ $\theta(\text{HCH}) \sim 133^\circ$ ] of the isolated  $\text{CH}_2$ . The Ni-C distance in the carbene is only  $0.053 \text{ \AA}$  shorter than the  $1.884 \text{ \AA}$  predicted with the same theoretical model for  $\text{Ni}(\text{CO})_4$ . This suggests that the formal double bond in  $(\text{CO})_3\text{Ni}=\text{CH}_2$  is relatively weak, in agreement with the findings of Rappe' and Goddard (55) for the naked  $\text{NiCH}_2$  molecule. The only experimentally known nickel carbene distance is the value  $r(\text{Ni}=\text{C}) = 1.909 \text{ \AA}$  found (56) for the ion  $[\text{Me}_2\text{NCSNiC}(\text{NMe}_2)\text{SC}(\text{NMe}_2)\text{S}]^+$ . A final energetic prediction is that the sixfold barrier to rotation about the Ni-C (methylene) axis is small,  $\sim 0.2 \text{ kcal}$ , in agreement with qualitative ideas about barriers of this general type (57).

Table IV shows a comparison of the Mulliken atomic populations of  $(\text{CO})_3\text{NiCH}_2$  and  $\text{Ni}(\text{CO})_4$ . It should be emphasized that while any given Mulliken atomic population is of questionable absolute value, the use of the same basis set and the same SCF procedure for the two molecules should make comparisons significant (44).

The larger positive charge on Ni in the carbene complex as opposed to  $\text{Ni}(\text{CO})_4$  is seen to be due to the negative charge (0.58) build-up on the electrophilic methylene carbon. This increased methylene carbon population resides to a high degree in the methylene p orbitals. The latter hold 3.00 Mulliken electrons, compared with only 2.22 for the carbon p orbitals of each C atom in  $\text{Ni}(\text{CO})_4$ . In this Mulliken picture the carbonyl carbons are consistently slightly positive ( $\sim +0.1$ ) in both  $(\text{CO})_3\text{NiCH}_2$  and  $\text{Ni}(\text{CO})_4$ , and their populations differ relatively little between the two molecules. There is, however, a slight shift from carbon s to p populations in the carbene complex relative to  $\text{Ni}(\text{CO})_4$ .

The dominant difference between the Ni atom charge distributions in  $(\text{CO})_3\text{NiCH}_2$  and  $\text{Ni}(\text{CO})_4$  is seen to lie with the 3d populations. The carbene complex has a population of 8.72 d electrons, while  $\text{Ni}(\text{CO})_4$  has 9.03. The difference,  $0.31 e^-$ , is remarkably close to the difference of 0.29 obtained by subtracting the total

Ni charges  $\text{Ni}^{+0.53}$  (carbene) -  $\text{Ni}^{+0.24}$  (tetracarbonyl). The Ni s population for the carbene (6.14) is slightly less than that (6.17) for  $\text{Ni}(\text{CO})_4$  while the opposite small difference is seen for the Ni p populations.

It is worth noting that while both  $(\text{CO})_3\text{NiCH}_2$  and  $\text{Ni}(\text{CO})_4$  are commonly referred to as  $d^{10}$  complexes, it is the Ni 4s and 4p which play an important role in the metal-ligand bonds. After the 12 electrons occupying the Ni 2p and 3p orbitals are discounted, there are still 0.61 and 0.57  $e^-$  occupying p functions for the two molecules. This ~0.6 electron can be attributed to nickel 4p participation, which is seen to be quite important. Certainly for the two molecules under discussion, 4p participation is much more important than 4s.

#### D. Bis (Cyclobutadiene)Nickel

Certainly one of the important achievements in synthetic organometallic chemistry in 1978 was the first cyclobutadiene sandwich compound. Hoberg, Krause-Göing and Mynott (58) used spectroscopic data and chemical data to identify the  $\text{Ni}(\text{C}_4\text{H}_4)_2$  molecule, which crystallizes as well-formed blue crystals. Since the observed octaphenyl compound is of low chemical reactivity, it is not inconceivable that the parent  $\text{Ni}(\text{C}_4\text{H}_4)_2$  might be synthesized in time.

Since our theoretical studies (23) of  $\text{Ni}(\text{C}_4\text{H}_4)_2$  are still in progress, a detailed report is not possible here. However, some mention is in order in light of the recent paper on ferrocene by Almlöf and colleagues (59). Lüthi, Ammeter, Almlöf, and Korsell optimized the metal-ring distance in  $\text{Fe}(\text{C}_5\text{H}_5)_2$  and found it to be 1.89 Å, much larger than the experimental distance (60), 1.65 Å. This poor agreement between SCF theory and experiment is surprising, so some discussion is in order. Almlöf used a Roos-type (15) basis of size  $\text{Fe}(12s\ 7p\ 4d/8s\ 5d\ 3d)$ ,  $\text{C}(7s\ 3p/4s\ 2p)$ ,  $\text{H}(4s/2s)$ . Such a basis will yield much higher absolute energies than those used here, but should otherwise be quite acceptable, with the exception of one possible deficiency. That is, the absence of a set of d functions more spatially extended than those required to describe the  $s^2d^6$  configuration of the iron atom.

The present theoretical study of  $\text{Ni}(\text{C}_4\text{H}_4)_2$  employed a  $\text{Ni}(14s\ 9p\ 6d/10s\ 6p\ 3d)$ ,  $\text{C}(10s\ 6p/6s\ 3p)$ ,  $\text{H}(5s/3s)$  basis set. Although no structural information is yet available for cyclobutadiene sandwiches, the metal-ring distance in nickelocene  $\text{Ni}(\text{C}_5\text{H}_5)_2$  is known from electron diffraction (60) to be  $1.83\ \text{\AA}$ . Our preliminary studies suggest for  $\text{Ni}(\text{C}_4\text{H}_4)_2$  a metal-ring distance of  $\sim 1.73\ \text{\AA}$ , which would certainly not appear to display the problem reported by Almlöf for ferrocene. In the near future we hope to complete the theoretical structure of  $\text{Ni}(\text{C}_4\text{H}_4)_2$ , by simultaneously optimizing the ring C-C distance and the tilt angle of the hydrogens with respect to the  $\square$  plane.

#### Concluding Remarks

It should be evident that theoretical predictions approaching the Hartree-Fock limit are beginning to appear for genuine organometallic molecules, such as  $\text{Ni}(\text{CO})_4$ ,  $\text{Ni}(\text{C}_2\text{H}_4)_3$ ,  $(\text{CO})_3\text{NiCH}_2$ , and  $\text{Ni}(\text{C}_4\text{H}_4)_2$ . We are confident that the 1980's will see many more such studies, and the latter will begin to have a significant impact upon organometallic chemistry.

#### Acknowledgements

The research discussed here was carried out in collaboration with Robert W. Hand, William J. Hunt, Diane M. Hood, Russell M. Pitzer, Jean Demuynck, Dale Spangler, John J. Wendoloski, Michel Dupuis, John D. Goddard, and Paul S. Bagus. This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract No. W-7405-Eng-48.

### Literature Cited

1. A number of interesting views of developments during this period are given in "Perspectives in Organometallic Chemistry," Volume 100, Journal of Organometallic Chemistry.
2. H. F. Schaefer, Accounts Chem. Res., 10 (1977) 287.
3. H. Ibach, S. Lehwald, J. Vacuum Sci. Technol., 15 (1978) 407.
4. L. L. Kesmodel, L. H. Dubois, G. A. Somorjai, J. Chem Phys., 70 (1979) 2180.
5. E. L. Muetterties, J. Stein, Chem. Revs., 79 (1979) 479.
6. J. E. Demuth, Surf. Sci., 93 (1980) L82.
7. H. F. Schaefer, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results"; Addison-Wesley: Reading, Massachusetts, 1972.
8. R. S. Milliken, C. C. J. Roothaan, Proc. Natl. Acad. Sci. (U.S.A.), 45 (1959) 394.
9. P. E. Cade, K. D. Sales, A. C. Wahl, J. Chem Phys., 44 (1966) 1973.
10. P. E. Cade, A. C. Wahl, Atomic Data Nuclear Data Tables, 13 (1973) 339.
11. I. Shavitt, "The Method of Configuration Interaction," Modern Theoretical Chemistry, 3 (1977) 189-275.
12. W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, J. A. Pople, Prog. Phys. Org. Chem., 11 (1974) 175.
13. See for example B. R. Brooks, W. D. Laidig, P. Saxe, H. F. Schaefer, J. Chem. Phys., 72 (1980) 3837.
14. A. J. H. Wachters, J. Chem. Phys., 52 (1970) 1033.
15. B. Roos, A. Veillard, G. Vinot, Theor. Chim. Acta, 20 (1971) 1.
16. B. R. Brooks, H. F. Schaefer, Mol Phys., 34 (1977) 193.
17. D. R. Yarkony, H. F. Schaefer, Chem. Phys. Lett., 15 (1972) 514.
18. R. W. Hand, W. J. Hunt, H. F. Schaefer, J. Amer. Chem. Soc., 95 (1973) 4517.
19. D. M. Hood, R. M. Pitzer, H. F. Schaefer, J. Chem. Phys., 71 (1979) 705.
20. R. M. Pitzer, H. F. Schaefer, J. Amer. Chem. Soc., 101 (1979) 7176.
21. J. Demuynck, H. F. Schaefer, J. Chem. Phys., 72 (1980) 311.
22. D. Spangler, J. J. Wendoloski, M. Dupuis, M. M. L. Chen, H. F. Schaefer, to be published.
23. R. M. Pitzer, J. D. Goddard, H. F. Schaefer, to be published.
24. W. C. Swope, H. F. Schaefer, Mol. Phys., 34 (1977) 1037.
25. P. J. Hay, J. Chem. Phys., 66 (1977) 4377.
26. T. H. Dunning, P. J. Hay, "Gaussian Basis Sets for Molecular Calculations," Modern Theoretical Chemistry, 3 (1977) 1-27.
27. A. E. Stevens, J. L. Beauchamp, J. Amer. Chem. Soc., 101 (1979) 6449.
28. T. H. Dunning, B. H. Botch, J. F. Harrison, J. Chem. Phys. 72 (1980) 3419.
29. A. Büchler, J. L. Stauffer, W. Klemperer, J. Chem. Phys., 40 (1964) 3471.
30. T. C. Devore, W. Weltner, J. Amer. Chem. Soc., 99 (1977) 4700.
31. P. S. Bagus, H. F. Schaefer, J. Chem. Phys., 58 (1973) 1844.
32. J. H. Yates, R. M. Pitzer, J. Chem. Phys., 70 (1979) 4049.
33. J. W. Hastie, R. H. Hauge, J. L. Margrave, J. Less-Common Metals, 39 (1975) 309.
34. K. P. Huber, G. Herzberg, "Constants of Diatomic Molecules"; Van Nostrand Reinhold: New York, 1979.
35. W. Hayes, P. O. McCarvill, T. E. Nevin, Proc. Phys. Soc. (London), 70 (1957) 904.
36. R. J. Van Zee, T. C. Devore, J. L. Wilkerson, W. Weltner, J. Chem. Phys., 69 (1978) 1869.
37. R. J. Van Zee, C. M. Brown, W. Weltner, Chem. Phys. Lett., 64 (1979) 325.



38. M. P. Guse, R. J. Blint, A. B. Kunz, *Int. J. Quantum Chem.*, 11 (1977) 725.
39. P. R. Scott, W. G. Richards, *J. Chem. Phys.*; 63 (1975) 1690.
40. B. K. Bower, H. G. Tennant, *J. Amer. Chem. Soc.*, 94 (1972) 2512.
41. P. O. Löwdin, *Advan. Chem. Phys.*, 2 (1959) 207.
42. E. R. Davidson, D. W. Silver, *Chem. Phys. Lett.*, 52 (1978) 403.
43. L. O. Brockway, P. C. Cross, *J. Chem. Phys.*, 3 (1935) 828.
44. L. Hedberg, T. Iijima, K. Hedberg, *J. Chem. Phys.*, 70 (1979) 3224.
45. K. Fischer, K. Jonas, G. Wilke, *Angew. Chem. Int. Ed. Engl.*, 12 (1973) 565.
46. N. Rösch, R. Hoffmann, *Inorg. Chem.*, 13 (1974) 2656.
47. M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 18 (1951) C79.
48. W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.* 17, (1978) 800.
49. E. O. Fischer, A. Maasböl, *Angew. Chem. Int. Ed. Engl.*, 3 (1964) 580.
50. R. Mason, *Israel J. Chem.*, 15 (1977) 174.
51. E. L. Mettertides, *Angew. Chem. Int. Ed. Engl.* 17 (1978) 545.
52. C. A. Tolman, *Chem. Soc. Revs.*, 1 (1972) 337.
53. R. R. Schrock, *J. Amer. Chem. Soc.*, 97 (1975) 6577
54. J. Schwartz, K. I. Gell, *J. Organomet. Chem.*, 184 (1980) C1.
55. A. K. Rappe, W. A. Goddard, *J. Amer. Chem. Soc.*, 99 (1977) 3966.
56. W. K. Dean, R. S. Charles, D. G. Van Derveer, *Inorg. Chem.*, 16 (1977) 3328.
57. T. A. Albright, R. Hoffmann, Y. C. Tse, T. D'Ottavio, *J. Amer. Chem. Soc.*, 101 (1979) 3812.
58. H. Hoberg, R. Krause-Göing, R. Mynott, *Angew. Chem. Int. Ed. Engl.*, 17 (1978) 123.
59. H. P. Lüthi, J. Ammeter, J. Almlöf, K. Korsell, *Chem. Phys. Lett.*, 69 (1980) 540.
60. L. Hedberg, K. Hedberg, *J. Chem. Phys.*, 53 (1970) 1228.

Table I. Large basis SCF predictions of Yates and Pitzer (32) for the equilibrium geometries and out-of-plane vibrational frequencies of the transition metal trifluorides.

M	M-F ( $\text{\AA}$ )	Vibrational frequency ( $\text{cm}^{-1}$ )	Geometry	Ground state
Sc	1.88	129.6	$D_{3h}$	$1A'_1$
Ti	1.83	140.6	$D_{3h}$	$(a'_1)^1 2A'_1$
V	1.81	152.0	$D_{3h}$	$(e'')^2 3A'_2$
Cr	1.77	113.2	$C_{3v}$	$e^2 a_1^1 4A_2$
Mn	1.77			$(e'')^2 (a'_1)^1 (e')^1 5E'$
Fe	1.78	179.3	$D_{3h}$	$(e'')^2 (a'_1)^1 (e')^2 6A'_1$
Co	1.75	190.5	$D_{3h}$	$(e'')^2 (a'_1)^2 (e')^2 5A'_1$
Ni	1.73	221.2	$D_{3h}$	$(e'')^4 (a'_1)^1 (e')^2 4A'_2$

Table II. Comparison of different contracted Gaussian basis sets in SCF calculations on tetrahedral  $\text{TiH}_4$  with bond distance  $r(\text{Ti-H}) = 3.2 a_0$ .

	Titanium basis	Hydrogen basis	Remarks	Energy (hartree)
1.	14s 9p 5d/10s 6p 2d	5s/3s	Original Wachters basis set	-850.57136
2.	14s 10p 5d/10s 7p 2d	5s/3s	Add p function ( $\alpha = 0.156$ ) to #1.	-850.58824
3.	13s 10p 5d/9s 7p 2d	5s/3s	Delete s basis function in #2 with smallest exponent	-850.58812
4.	13s 10p 5d/9s 7p 2d	4s/2s	Use smaller hydrogen s set than in #3	-850.57926
5.	14s 10p 5d/10s 7p 2d	5s 1p/3s 1p	Add and optimize ( $\alpha = 0.5$ ) p functions on hydrogen	-850.60089
6.	14s 11p 5d/10s 8p 2d	5s 1p/3s 1p	Add second p basis function ( $\alpha = 0.0611$ ) to describe Ti 4p	-850.60096
7.	14s 11p 6d/10s 8p 3d	5s 1p/3s 1p	Add diffuse d function ( $\alpha = 0.072$ ) to #6	-850.60127

Table III. Bond distances and energetic information for tetrahedral transition metal hydride molecules.

Electronic state	$r_e$ (M-H), (Å)	Relative energy (kcal/mol)	Self-consistent field dissociation energy (kcal/mol)
TiH <sub>4</sub> $^1A_1$	1.696	0	132
VH <sub>4</sub>	$^2E$ (e)	0	86
	$^2T_2(t_2)$	+36	
CrH <sub>4</sub>	$^3A_2(e^2)$	0	65
	$^1E(e^2)$	47	
	$^3T_1(t_2^2)$	90	
	$^1A_1(e^2)$	92	
MnH <sub>4</sub>	$^4T_1(t_2e^2)$	0	-36
	$^2E(e^3)$	19	
FeH <sub>4</sub>	$^5T_2(t_2^2e^2)$	0	0
	$^1A_1(e^4)$	23	
	$^5E(t_2^3e)$	48	
	$^3A_2(t_2^2e^2)$	88	
CoH <sub>4</sub>	$^6A_1(t_2^3e^2)$	0	27
	$^4A_1(t_2^3e^2)$	36	
	$^2T_2(t_2e^4)$	67	
	$^4T_1(t_2^3e^2)$	89	
NiH <sub>4</sub>	$^5T_2(t_2^4e^2)$	0	18
	$^5E(t_2^3e^3)$	11	
	$^3T_1(t_2^2e^4)$	51	
	$^1A_1(t_2^2e^4)$	115	
	$^3A_2(t_2^4e^2)$	122	

Table IV. Selected mulliken populations for the prototype nickel carbene complex and nickel tetracarbonyl.

	$(\text{CO})_3\text{NiCH}_2$	$\text{Ni}(\text{CO})_4$
Nickel		
s	6.04	6.06
p	12.61	12.58
d	8.82	9.13
total	27.47	27.77
Methylene C		
s	3.58	
p <sub>x</sub>	0.47	
p <sub>y</sub>	1.05	
p <sub>z</sub>	1.48	
total	6.58	
Hydrogen		
s	0.85	
Carbonyl C		
s	3.60, 3.65, 3.65	3.67
p	2.28, 2.27, 2.27	2.23
total	5.89, 5.92, 5.92	5.90
Oxygen		
s	3.80, 3.80, 3.80	3.79
p	4.38, 4.38, 4.38	4.37
total	8.17, 8.17, 8.17	8.15

Figure Captions

- Figure 1. Walsh-like diagram constructed from the six highest orbital energies of  $\text{ZnF}_2$  as a function of bond angle.
- Figure 2. Diagram of  $\text{FeF}_3$  orbital energies for those orbitals corresponding to the d orbitals of  $\text{Fe}^{3+}$  in a crystal field picture.
- Figure 3. Bond angle sensitive molecular orbitals for  $\text{MH}_2$ . The left hand side of the figure refers to a bond angle of  $\sim 130^\circ$  and the right hand side to  $180^\circ$  (linear).
- Figure 4. Total energies of  $\text{NiH}_2$ ,  $\text{MnH}_2$ , and  $\text{TiH}_2$  as a function of  $\text{HMH}$  bond angle. This figure illustrates the increasing flatness of the  $\text{MH}_2$  potential energy surfaces as one moves to the left in the periodic table across the first-row transition metals M.
- Figure 5. Geometries of the "planar" and "upright" conformations of tris ( $\eta^2$ -ethylene) nickel (0).
- Figure 6. Extended Hückel one-electron energies (46) for the three highest occupied molecular orbitals of  $\text{Ni}(\text{C}_2\text{H}_4)$  as a function of rotation between the planar and upright conformers.
- Figure 7. Structural assumptions for the prototype nickel carbene complex. The three CO ligands are assumed to be tetrahedrally coordinated about the nickel atom.

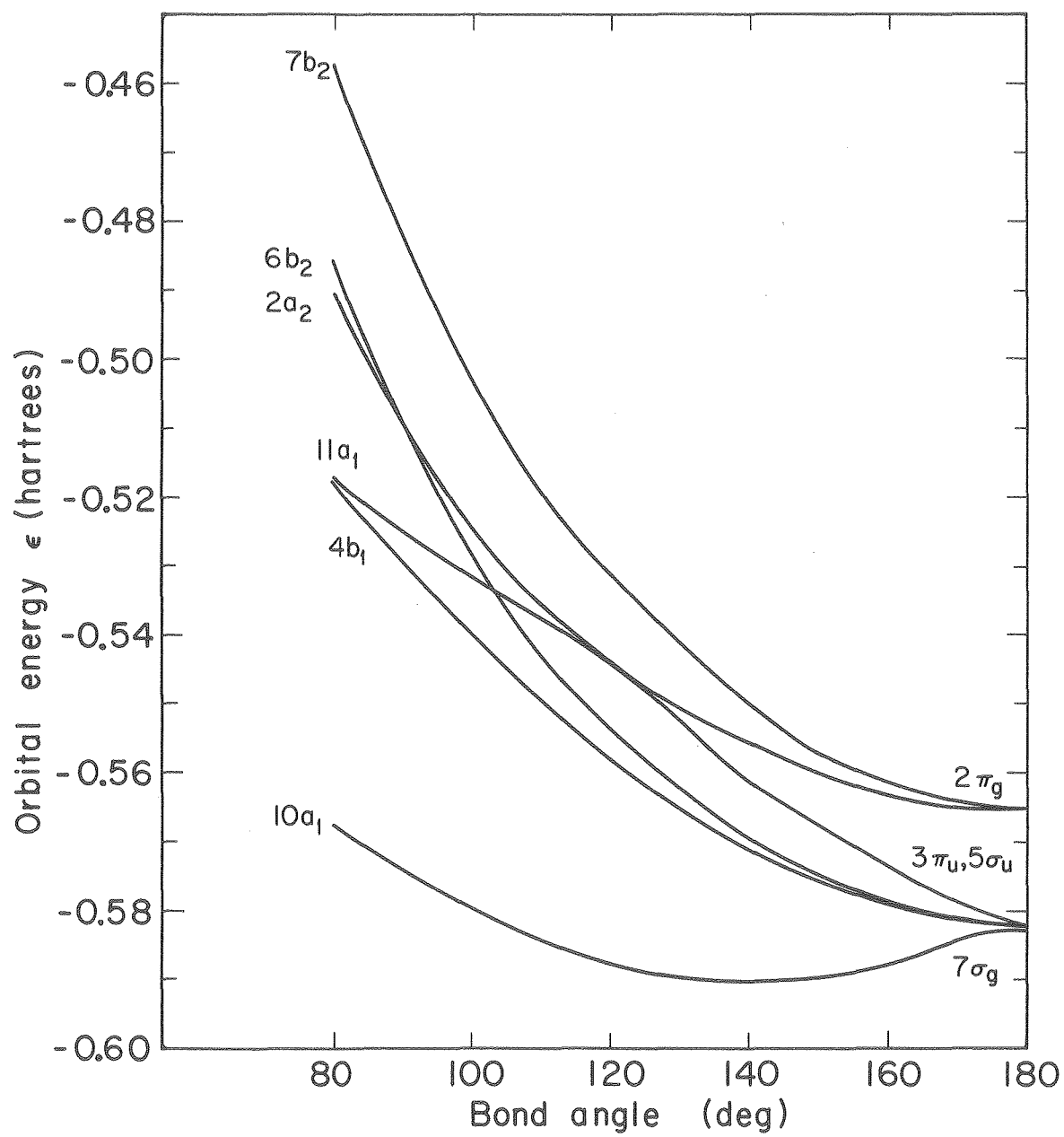
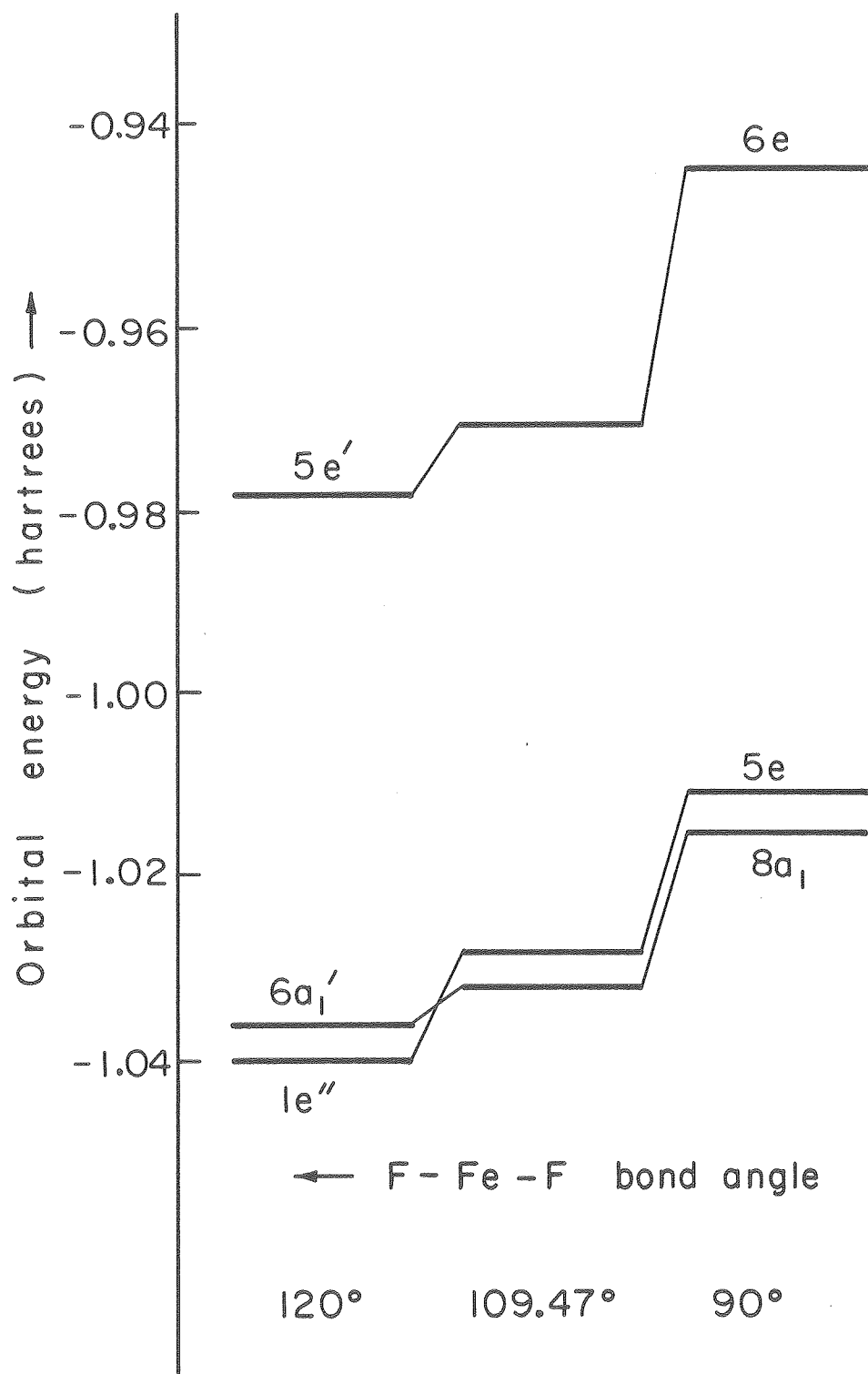


Figure 1



XBL7211 - 4374

Figure 2



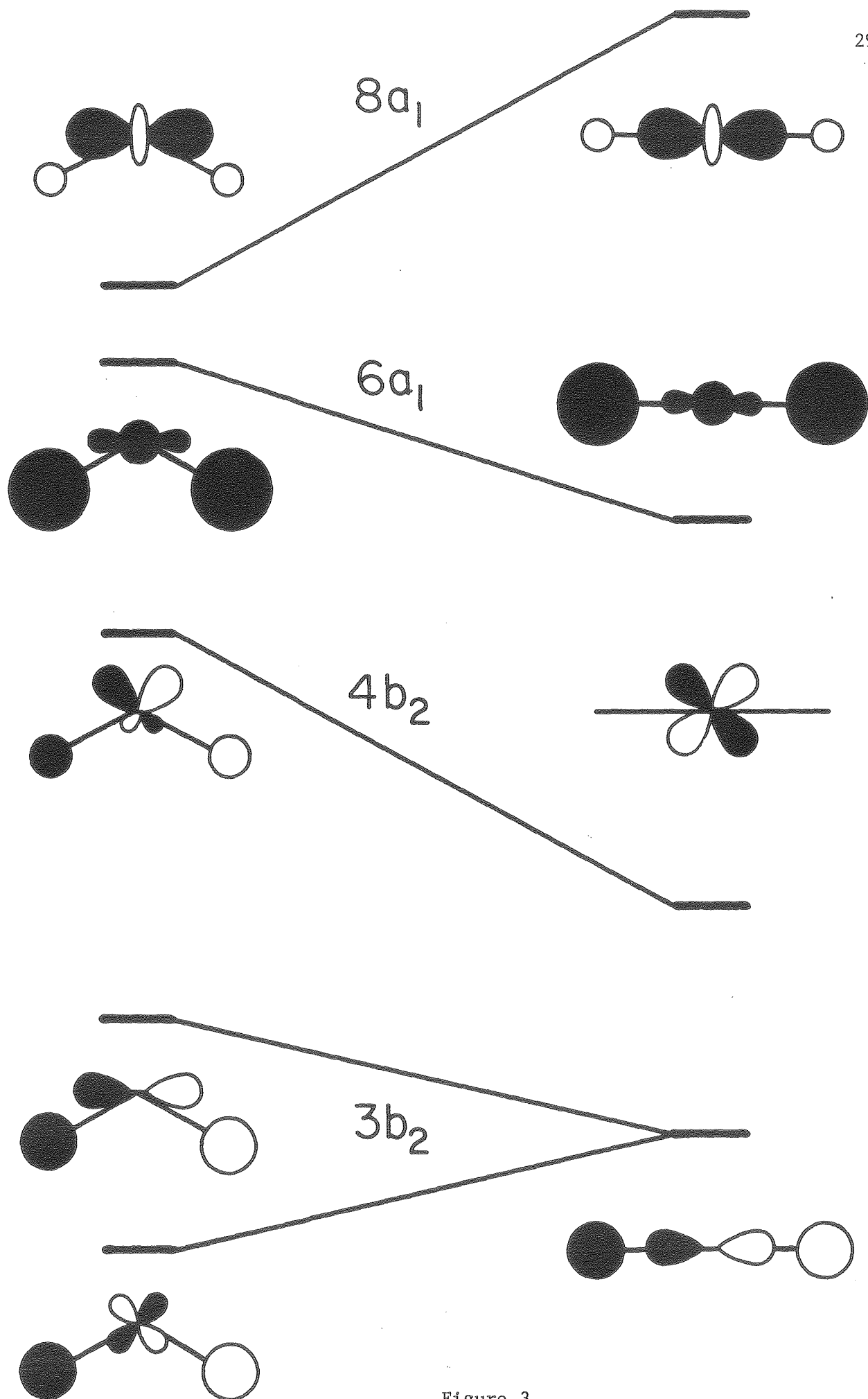


Figure 3

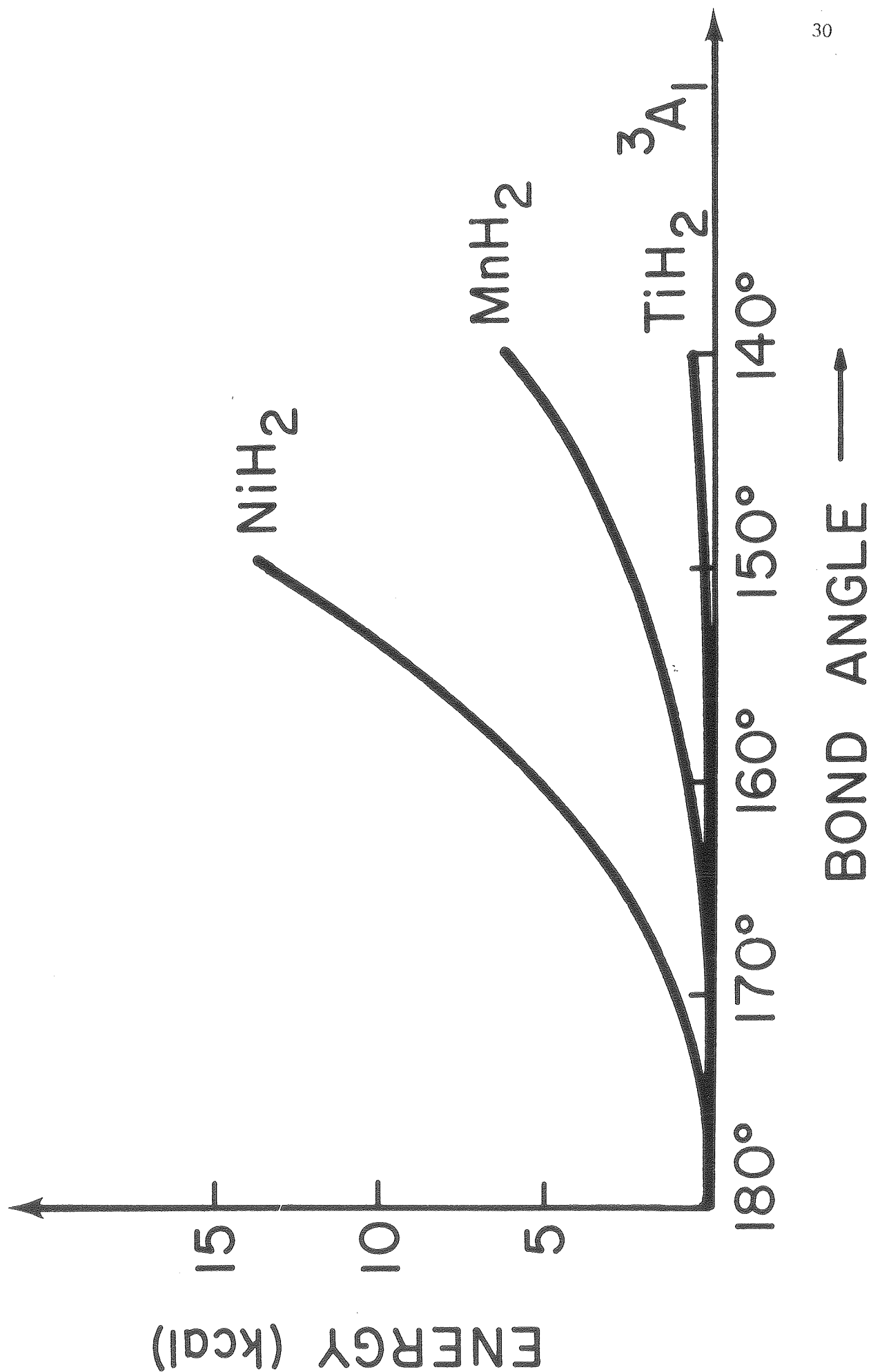
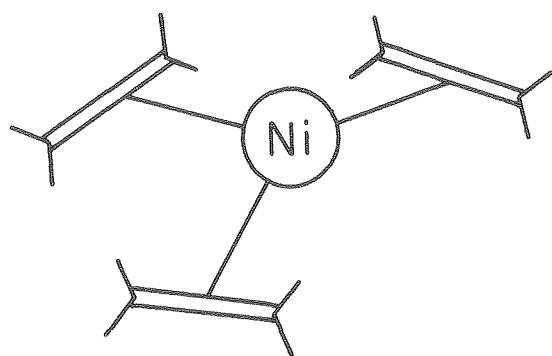
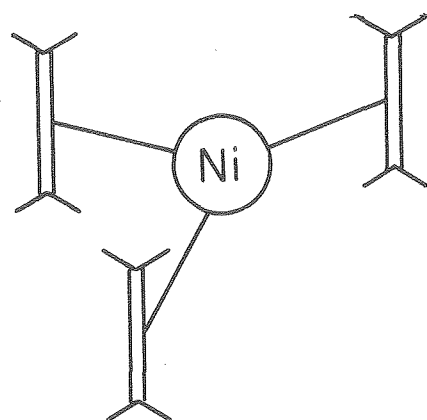


Figure 4



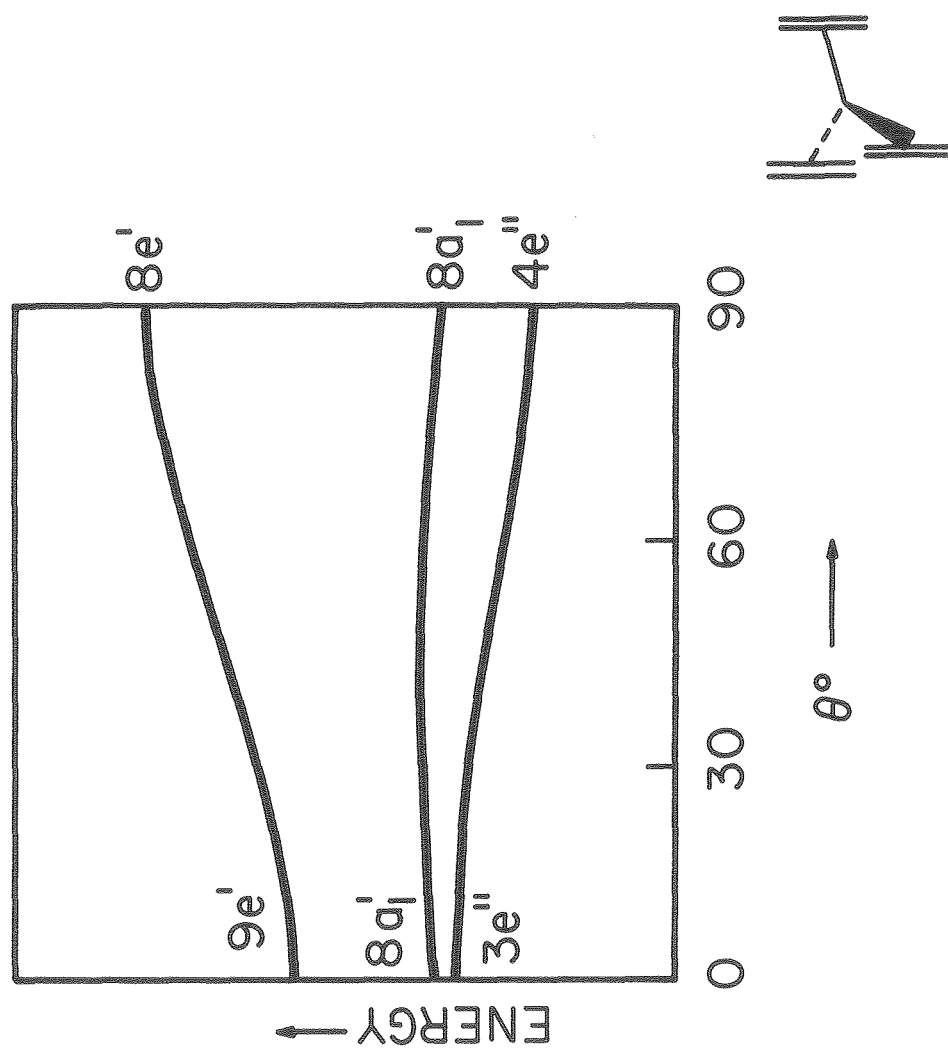
PLANAR



UPRIGHT

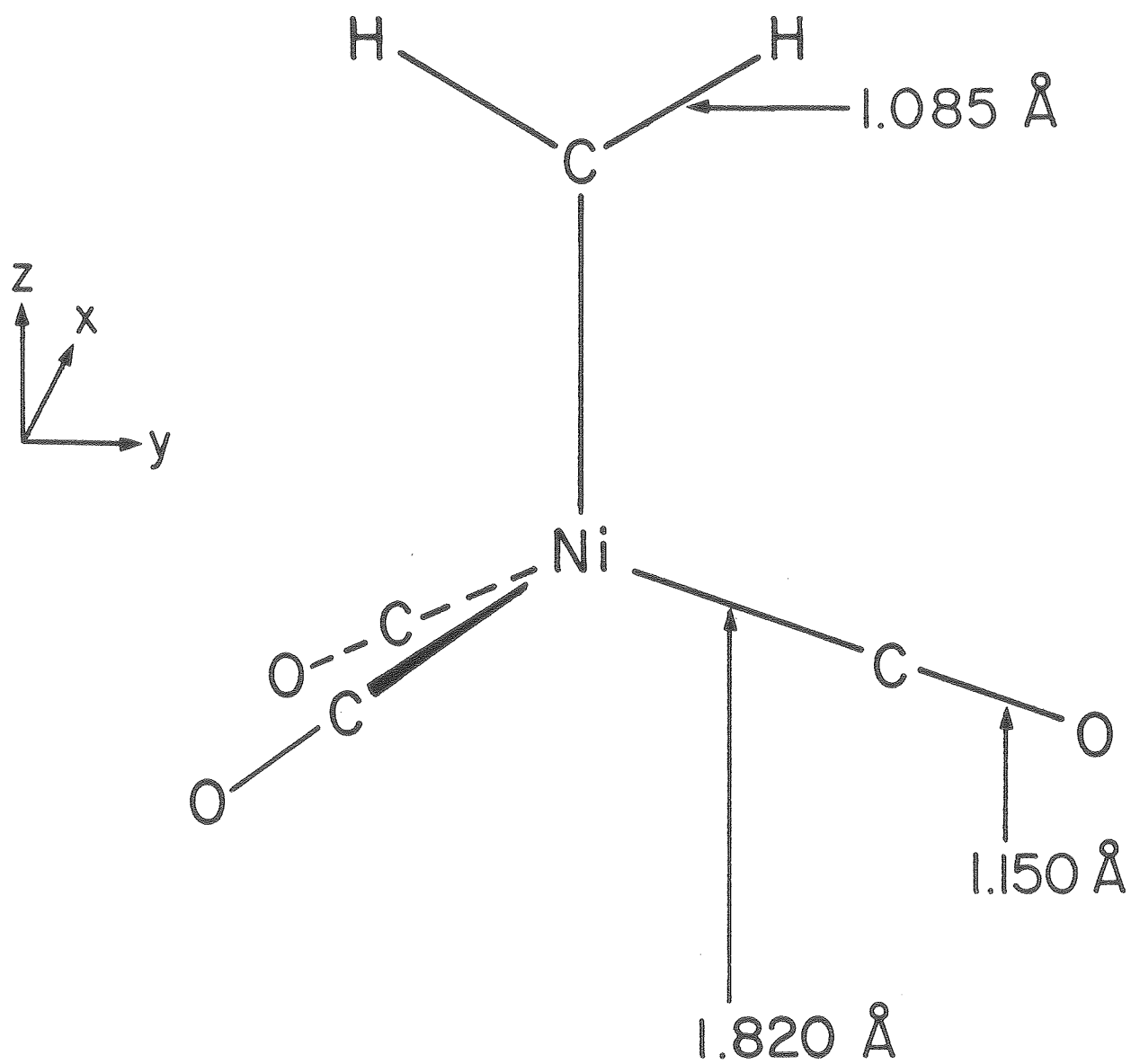
XBL 793-8747

Figure 5



XBL 797-10484

Figure 6



XBL 803-8756

Figure 7

